Cycloheptatriene and Tropylium Metal Complexes. Part IX.[1] [1,5] Hydrogen Migrations in Cycloheptatrienes complexed to Chromium

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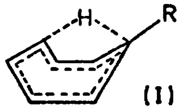
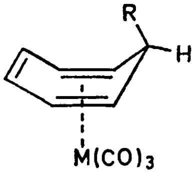
Specific migration of the ψ-equatorial 7-*endo*-hydrogen atom in tricarbonylchromium complexed cycloheptatrienes has been confirmed using the 7-*exo*- and -*endo*-phenyl derivatives and the approximate rates of migration have been determined for the 7-*exo*-methyl and -*p*-tolyl complexes. In all cases sequential [1,5] migration is shown to occur giving first the 3-, then 1-, and finally 2-substituted products. In the 7-methyl case the energy of activation for rearrangement is considerably lower in the complex than in the free ligand, but the difference is much smaller in the case of aryl substituents. These findings are discussed in relation to a possible mechanism for the rearrangement reaction of the complexes.

CYCLOHEPTATRIENE and its derivatives undergo a ready, thermal [1,5] hydrogen migration.[2] Numerous studies have been undertaken to determine the kinetics of the process, now generally agreed to be unimolecular and first order in the cycloheptatriene species, and various estimates of the associated thermodynamic quantities have been made.[3-6] Eggers [3] has discussed the process in terms of a transition state (I), in which the cycloheptatriene ring is ' bent ' to allow the migrating hydrogen atom to become simultaneously bonded to the two appropriate sites. Clearly, the migrating hydrogen atom must be in an axial position prior to such a transition state. A similar rearrangement occurs in cycloheptatriene complexed to metal, *e.g.* (II; M = Cr or Mo), and it was shown [7] that, in contrast to the free ligand case, only the hydrogen atom in the 7-*endo*-position, which is ψ-equatorial, is able to migrate. This has now been supported by the observation that 7-*endo*-substituted cycloheptatriene complexes do not undergo rearrangement, whilst those having only a 7-*exo*-substituent do.[8]



(I)

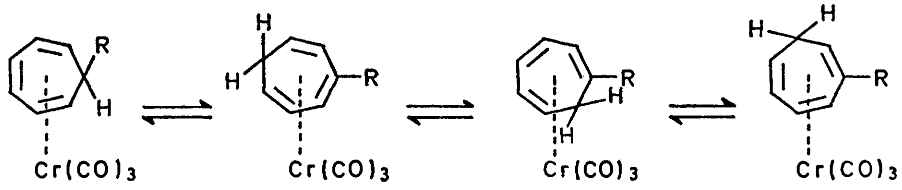


(II) a; R = Me, M = Cr
b; R = *p*-Tolyl, M = Cr
c; R = Ph, M = Cr

On the basis of studies on deuterium-labelled molybdenum compounds for which essentially complete deuterium scrambling occurred, it was suggested that a possible mechanism for the process might involve initial migration of the hydrogen to the metal with formation of a tropylium molybdenum hydride species, $C_7H_7Mo(H)(CO)_3$ in which the ring positions are equivalent.[7] Contrary to this, we have now shown that the overall process involves a series of sequential [1,5] hydrogen migrations (Scheme).

For the complexes (IIa) and (IIb) it was possible to isolate the first-formed product in each case. N.m.r. evidence clearly indicates that they are 3-substituted cycloheptatriene complexes (III). The subsequent stages of the reaction were followed by monitoring the appearance of new methyl peaks in the spectra on further heating. For the case of (IIc) it was possible to isolate the 3-phenyl isomer, and also the subsequently formed 1-phenyl complex (IV). This latter compound was identified from its n.m.r. spectrum and appropriate spin decoupling experiments.

The rate of the [1,5] isomerisation was measured by monitoring the disappearance of the methyl resonance of suitable complexes. In general this rearrangement was seen qualitatively to be rather faster than is the case with the free ligand species.



(III) (IV)

SCHEME

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[2] G. Büchi and E. M. Burgess, *J. Amer. Chem. Soc.*, 1962, **84**, 3104.

[3] K. W. Eggers, *J. Amer. Chem. Soc.*, 1969, **89**, 3688.

[4] A. P. Ter Borg and H. Kloosterziel, *Rec. Trav. chim.*, 1963, **82**, 741.

[5] A. P. Ter Borg, H. Kloosterziel, and N. Van Meurs, *Rec. Trav. chim.*, 1963, **82**, 725.

[6] R. W. Murray and M. L. Kaplan, *J. Amer. Chem. Soc.*, 1966, **88**, 3527.

[7] W. R. Roth and W. Grimme, *Tetrahedron Letters*, 1966, 2347.

[8] A preliminary account of this work has been published. M. I. Foreman, G. R. Knox, P. L. Pauson, K. H. Todd, and W. E. Watts, *Chem. Comm.*, 1970, 843.

The rate of the isomerisation of the 7-*exo*-substituted cycloheptatriene complex (7-R) to the 3-substituted species (3-R) was further studied in a more quantitative way, again by monitoring the intensity of the methyl resonance absorption for (IIa) and (IIb). If each step of the overall rearrangement is discussed in terms of first order-kinetics [equation (1)] and if $k_{-1} \ll k_1$ then

$$\text{7-R} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{3-R} \rightleftharpoons \text{further products} \qquad (1)$$

the observed diminuition of the 7-R resonance can be regarded as a straightforward exponential decay [equation (2)].

$$[\text{7-R}]_t = [\text{7-R}]_0\, e^{-k_1 t} \qquad (2)$$

The assumption was checked by monitoring the behaviour of pure samples of the 3-Me- and 3-(*p*-tolyl)-cycloheptatriene chromium tricarbonyl complexes on heating to 100° in an n.m.r. tube. In both cases resonances attributable to further rearrangement products formed rapidly. The 7-*exo*-isomer, however, was detected in the spectrum only after approximately 48 h, the ratio of the 7-*exo*-isomer to the other isomeric species being approximately 1 : 100 at equilibrium; k_{-1} may therefore be neglected.

The data obtained from a series of experiments, each carried out over a period of time approximating to at least one half-life for the particular conditions studied, were therefore fitted to the exponential decay function [equation (2)] by a modification of the least-squares computer program described by Wolberg.[9] An error analysis was included in the program, errors quoted in every case are for a 70% ' confidence interval '.

RESULTS

Rate constants and derived thermodynamic quantities for the complexes (IIa) and (IIb) are given in the Table. Values for the rate constants appropriate to (IIa) in CD_3OD solution, and for tricarbonyl-(2-methyl-7-*exo*-*p*-tolylcycloheptatriene)chromium in benzene, are also included.

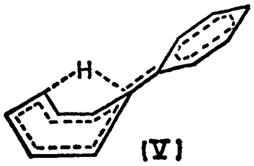
Variation of rate constant with temperature

T/°C	k_1/s^{-1}
(*a*) 7-*exo*-Methyl complex (IIa), benzene solution	
101·5	$(3{\cdot}20 \pm 0{\cdot}05) \times 10^{-4}$
91·5	$(1{\cdot}30 \pm 0{\cdot}05) \times 10^{-4}$
81·5	$(3{\cdot}20 \pm 0{\cdot}02) \times 10^{-5}$
77·0	$(4{\cdot}1 \pm 0{\cdot}7) \times 10^{-5}$
71·5	$(1{\cdot}8 \pm 0{\cdot}4) \times 10^{-5}$
$E_A = 24{\cdot}2 \pm 1{\cdot}6$ kcal mol^{-1}	$\log_{10} A = 10{\cdot}6 \pm 1{\cdot}4$
(*b*) 7-*exo*-(*p*-Tolyl) complex (IIb), benzene solution	
96·0	$(5{\cdot}00 \pm 0{\cdot}04) \times 10^{-4}$
92·0	$(3{\cdot}30 \pm 0{\cdot}08) \times 10^{-4}$
81·5	$(1{\cdot}10 \pm 0{\cdot}04) \times 10^{-4}$
72·0	$(3{\cdot}58 \pm 0{\cdot}15) \times 10^{-5}$
61·5	$(1{\cdot}14 \pm 0{\cdot}04) \times 10^{-5}$
$E_A = 27{\cdot}4 \pm 1{\cdot}2$ kcal mol^{-1}	$\log_{10} A = 12{\cdot}9 \pm 1{\cdot}0$
(*c*) 7-*exo*-Methyl complex (IIa), CD_3OD solution	
91·5	$(1{\cdot}14 \pm 0{\cdot}03) \times 10^{-4}$
(*d*) Tricarbonyl-(2-methyl-7-*exo*-*p*-tolylcycloheptatriene)chromium, benzene solution	
81·5	$(1{\cdot}60 \pm 0{\cdot}07) \times 10^{-4}$

With regard to the values quoted in the Table, it appears that the activation energy for the 7-*exo*-methyl complex (IIa) is slightly lower than that for (IIb). The A values on the other hand are not distinguished by this experiment, and may in fact be the same. The effect of changing the solvent from benzene to methanol, at least for the case of (IIa), is clearly very slight, and is consistent with the behaviour reported for rearrangements of the uncomplexed ligands.[4]

Comparing the activation energy for rearrangement of (IIa) with that quoted by Eggers [3] for the free ligand case in the gas phase ($E_A = 33{\cdot}25 \pm 0{\cdot}19$ kcal mol^{-1}), indicates fairly conclusively that the observed increase in the rate of the rearrangement for the metal-complexed species stems from a considerable reduction (*ca.* 9 kcal mol^{-1}) in this quantity. This is perhaps offset slightly by a reduction in the pre-exponential factor (A), implying an increased negative value for the entropy of activation.

No information is available for the uncomplexed 7-*p*-tolylcycloheptatriene rearrangement. However, an activation energy has been reported [5] for the [1,5] isomerisation of 7-phenylcycloheptatriene, which is considerably lower than values reported for other cycloheptatrienes.[4,5] It is argued that conjugative stabilisation becomes possible when the cycloheptatriene ring adopts the configuration (V)



(V)

suggested for the transition state. The increased, negative entropy of activation also reported for this particular rearrangement lends some support to the suggestion. If we assume that the rate enhancement observed in the complexed cycloheptatrienes is general, then clearly there is no additional enhancement of the rate from any source for the case of complex (IIb). This suggests that, for rearrangement of the metal complexes, the transition state is unlike that for the free ligand case, in so far as there is no conjugative stabilisation from overlap of orbitals of a benzene ring in the 7-position with π orbitals of the cycloheptatriene ring. In other words, compared to the free ligand, the transition state for the complex must be more like the starting material and less like the product. Beyond this conclusion no detailed mechanistic deduction can be based on this evidence.

In postulating a mechanism we are therefore guided solely by the stepwise nature and stereospecificity of the rearrangement. If a metal hydride intervenes, as postulated by Roth and Grimme [7] it must do so without allowing the ring carbons, even in the unsubstituted complexes (II; R = H), to become equivalent. A possible formulation for such a hydride is (VI) in which specific addition of the hydrogen atom to the end of the diene system would lead to the observed direction of the reaction. Although presumably fluxional, a short-lived intermediate of this type (VI) cannot be ruled out, since the rates of fluxional motion of the only known analogues differ widely {the n.m.r. spectra of the ionic iron complex [10] $[(CO)_3FeC_7H_7]^+$ and

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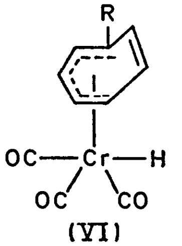
[9] J. R. Wolberg, ' Prediction Analysis,' Van Nostrand, New York, 1967.

[10] J. E. Mahler, D. A. K. Jones, and R. Pettit, *J. Amer. Chem. Soc.*, 1964, **86**, 3589.

the neutral manganese analogue $(CO)_3MnC_7H_7$ are characterised by coalescence temperatures [11] of *ca.* −50° and +27° respectively}. However we suggest that a much more probable course of reaction involves a related transition state, which we formulate as (VII), rather than a discrete intermediate. The ring distortion required to reach such a transition state is not dissimilar from that involved in the ring inversion which has been well studied in the uncomplexed cycloheptatrienes. In the complexes the ring is initially more nearly planar [12] and inversion should not therefore require excessive expenditure of energy. Substituents in the 1-position are known [13] to hinder such inversion and it may be significant that we find that tricarbonyl-(1,2,6,7-*exo*-tetraphenylcycloheptatriene)chromium (VIII) is readily formed by hydrogen migration from the 2,3,4,5-isomer but does not undergo further rearrangement even after prolonged heating at 100° in benzene.



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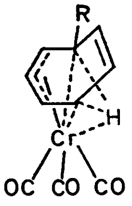
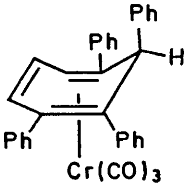


(VII)

As mentioned above, one of the compounds whose isomerisation was studied briefly was tricarbonyl-(2-methyl-7-*exo*-*p*-tolylcycloheptatriene)chromium. This was obtained from tricarbonyl(methyltropylium)chromium tetrafluoroborate by the successive addition of methoxide ion and its replacement with *p*-tolylmagnesium bromide. Although the direction of this reaction is that expected as the preferred mode from our previous work,[1] the exclusive formation of the 2-isomer shows a surprisingly strong apparent directive effect of the methyl substituent.



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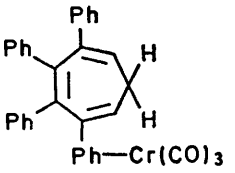

(IX)

EXPERIMENTAL

N.m.r. spectra were recorded at 60·004 MHz using a Perkin-Elmer R10 n.m.r. spectrometer equipped with a variable temperature probe. The temperature within the probe was monitored by means of a thermocouple to an accuracy of ±0·1°. Venner Electronics frequency and time measuring equipment was used for the measurement of time intervals during kinetic runs. Sample solutions for such runs were filtered through charcoal into n.m.r. tubes, purged thoroughly with nitrogen, and the tubes were subsequently sealed. All computational work relating to the kinetic studies was carried out on an ICT 1905 computer. High resolution mass spectra were obtained from an A.E.I. MS9 mass spectrometer operating on-line to an Elliott 905 computer. Peaks so measured were then assigned by an ' element map ' program.[14]

Materials.—Benzene was AnalaR grade, dried over sodium, and used without further purification. CD_3OD was used as supplied by CIBA A.R.L. The cycloheptatriene complexes were prepared by general methods described elsewhere,[15] and confirmed by high resolution mass and n.m.r. spectrometry. Each sample was recrystallised twice from light petroleum (b.p. 60—80°) at −70° and dried over $CaCl_2$ prior to use.

Tricarbonyl-(7-exo-*methylcycloheptatriene*)*chromium* (IIa). This was prepared as previously [15] and had τ (CS_2) 4·13 (2H, m, 3- and 4-H), 4·8—5·4 (2H, m, 2- and 5-H), 6·30 (2H, t, 1- and 6-H), 7·00 (1H, m, 7-*endo*-H), and 9·92 (3H, d, Me).

Tricarbonyl-(7-exo-p-*tolylcycloheptatriene*)*chromium* (IIb). Tricarbonyl-(7-*exo*-methoxycycloheptatriene)chromium (1·0 g) was added to *p*-tolylmagnesium bromide [from magnesium (0·2 g) and *p*-bromotoluene (1·2 g)] in ether (20 ml). Excess of Grignard reagent was discharged by addition of 10% methanol in ether. After evaporation the residue was extracted with benzene (200 ml). The concentrated filtrate was chromatographed on neutral alumina (deactivated over 6 h). Elution with a 10% solution of benzene in light petroleum (b.p. 60—80°) gave the *product* (IIb) (0·52 g, 45%), orange, crystals, m.p. 140° (Found: C, 64·5; H, 4·6%; *M*, 319·0359. $C_{17}H_{14}CrO_3$ requires C, 64·2; H, 4·4%; *M*, 319·0348), τ (CS_2), 3·34 (4H, ABq, C_6H_4), 4·14 (2H, m, 3- and 4-H), 5·14 (2H, m, 2- and 5-H), 5·74 (1H, t, 7-*endo*-H), 6·14 (2H, t, 1- and 6-H), and 7·87 (3H, s, Me).

Tricarbonyl-(*2-methyl-*7-exo-p-*tolylcycloheptatriene*)*chromium*. Tricarbonyl(methyltropylium)chromium tetrafluoroborate (1·7 g) was treated with excess of sodium methoxide (0·4 g) in methanol (20 ml). The resulting solution was evaporated at 0°, the residue extracted with ether (20 ml), and the ether solution then added to *p*-tolylmagnesium bromide [from magnesium (0·3 g) and *p*-bromotoluene (1·8 g)]. Excess of Grignard reagent was discharged by addition of methanol (10%) in ether. The solution was filtered and the residue was extracted with benzene (100 ml). The collected extracts were evaporated and the residue (0·5 g) chromatographed on neutral alumina. Elution of the the product with benzene (10%) in light petroleum (b.p. 60—80°) gave one fraction (0·45 g, 25%), orange crystals, m.p. 89—91°. This material appears to be a single isomer, identified as *tricarbonyl-*(*2-methyl-*7-exo-p-*tolylcycloheptatriene*)*chromium* from its n.m.r. spectrum, τ (CS_2) 3·37 (4H, ABq, C_6H_4), 4·29 (2H, m, 3- and 4-H), 5·25 (1H, t, 5-H), 5·80—6·30 (3H, m, 1-, 6-, and 7-*endo*-H), and 7·83 (3H, s, Me), 7·94 (3H, s, Me), (Found: C, 65·3; H, 5·2%; *M*, 333·0537. $C_{18}H_{16}CrO_3$ requires C, 65·0; H, 4·8%; *M*, 333·0506). The rearrangement of this complex was followed by monitoring the decay of the methyl resonance at τ 7·83, the peak at τ 7·94 becoming obscured by a methyl resonance of the product. The presence of an additional group in the cycloheptatriene ring means, in principle, that a greater number of possible isomeric products will result from sequential [1,5] hydrogen migrations, and accordingly the

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[11] T. H. Whitesides and R. A. Budnik, *Chem. Comm.*, 1971, 1514.

[12] P. E. Baikie and O. S. Mills, *J. Chem. Soc.* (*A*), 1968, 2704.

[13] W. E. Heyd and C. A. Cupas, *J. Amer. Chem. Soc.*, 1969, **91**, 1559.

[14] P. Bladon and M. I. Foreman, to be published.

[15] P. L. Pauson, G. H. Smith, and J. H. Valentine, *J. Chem. Soc.* (*C*), 1967, 1057, 1061.

n.m.r. spectrum of the equilibrated material was very complex. An attempt was made to chromatograph the product mixture, obtained by heating tricarbonyl-(2-methyl-7-*exo*-*p*-tolylcycloheptatriene)chromium at 110° for 8 h, on neutral alumina. Elution with 10% benzene in light petroleum (b.p. 60—80°) gave a mixture of two materials which were tentatively assigned the structure tricarbonyl-(2-methyl-4-*p*-tolylcycloheptatriene)chromium and tricarbonyl-(4-methyl-2-*p*-tolylcycloheptatriene)chromium on the basis that two doublets occur at τ 3·96 and 4·16 assignable to the two 4-protons. A second fraction was not identified. The final fraction again appeared to be a mixture of products, predominant however in the spectrum is a doublet at τ 6·91 (*J ca.* 12 Hz) which may be assigned to 7-*endo*-H of tricarbonyl-(6-methyl-1-*p*-tolylcycloheptatriene)chromium. These assignments are only tentative, since complete separation was not achieved.

Tricarbonyl-(1,2,6,7-exo-*tetraphenylcycloheptatriene*)*chromium* (VIII). 2,3,4,5-Tetraphenylcycloheptatriene[16] (0·4 g) was heated under reflux with excess of trisacetonitrile-(tricarbonyl)chromium[17] (0·8 g) in tetrahydrofuran (200 ml) for 1 h. After evaporation the product was chromatographed on neutral alumina (deactivated over 6 h). Two major fractions were eluted by benzene (80%) in light petroleum (b.p. 60—80°). The first fraction was identified as the *product* (VIII) (0·14 g, 30%), deep purple needles, m.p. 140—141° (Found: C, 75·8; H, 5·2%; *M*, 532·1182. $C_{34}H_{24}CrO_3$ requires C, 76·6; H, 4·6%; *M*, 532·1130), τ (CS_2) 2·6—3·0 (20H, m, Ph), 4·23 (2H, d, 3- and 5-H), 4·38 (1H, s, 7-*endo*-H), and 4·54 (1H, t, 4-H). The low-field position of the 7-*endo*-H is attributed to the effect of the adjacent, sterically crowded, phenyl groups. Further elution gave a second product, isomeric with the first (15 mg, 3%), yellow crystals, m.p. 180—182° (Found: *M*, 532·1136), identified from its n.m.r. spectrum as (IX) τ (CS_2) 2·9—3·4 (15H, m, Ph), 3·82 (1H, t, 6-H), 4·26 (1H, t, 1-H), 4·8—5·1 (5H, m, Ph–Cr), and 7·1—7·7br (2H, s, 7-*exo* and 7-*endo*-H).

Tricarbonyl-(1,2,6,7-*exo*-tetraphenylcycloheptatriene)-chromium (50 mg) in benzene (0·7 ml) was maintained at 110° for 4 h in a sealed n.m.r. tube. The behaviour of the complex on heating was monitored by recording the n.m.r. spectrum at suitable intervals. No change whatever was observed in the spectrum throughout this period.

Thermal Isomerisation of Tricarbonyl-(7-exo-*phenylcycloheptatriene*)*chromium* (IIc).—(a) The complex (IIc) (0·4 g) was refluxed in cyclohexane (50 ml) under nitrogen for 1·5 h. The solvent was removed and the residue chromatographed on silica gel. Light petroleum (b.p. 40—60°)–benzene (9 : 1) eluted two bands which yielded red crystalline solids in approximately equal amounts. The first solid had m.p. 85·5—86·5° and was shown by mixed m.p. (85·5—86·5°) and i.r. comparison to be identical with the 3-isomer described below. The second, m.p. 130—131°, was similarly shown to be the unchanged 7-*exo*-isomer. Thus the first step of isomerisation was *ca.* 50% complete under these conditions.

(b) The complex (IIc) (0·5 g) was refluxed in methylcyclohexane (100 ml) under nitrogen for 4 h. The solvent was removed and the residue chromatographed on a 6 ft column of alumina. Elution with light petroleum (b.p. 30—40°) yielded two crystalline products in a ratio *ca.* 1 : 2. The first, orange-red solid, m.p. 85·5—87° [from light petroleum (b.p. 30—40°) at −70°], was shown to be *tricarbonyl*-(3-*phenylcycloheptatriene*)*chromium* (IIIc) by its n.m.r. spectrum, τ ($CDCl_3$) 2·38 (5H, m, Ph), 3·60 (1H, dd, 4-H $J_{4,5}$ 7 Hz) 4·92br (2H, 4 × m, 2- and 5-H), 6·55 (2H, m, 1- and 6-H), 7·06 (1H, m, 7-*endo*-H), and 8·08br (1H, 2 × m, 7-*exo*-H), the most significant feature being the doublet (finely split by long-range coupling) at τ 3·6, at lowest field of the olefinic protons and unambiguously assignable to a single proton at the 4-position, so that C-3 must be substituted (Found: C, 63·3; H, 4·0. $C_{16}H_{12}CrO_3$ requires C, 63·15; H, 4·0%). The second fraction gave deep purple crystals, m.p. 78—78·5° [from light petroleum (b.p. 30—40°) at −70°] of *tricarbonyl*-(1-*phenylcycloheptatriene*)*chromium* (IVc), similarly identified by the presence of only one high-field olefinic proton in its n.m.r. spectrum, τ (CS_2) 2·71 (5H, s, Ph), 4·06 (2H, m, 3- and 4-H), 6·00 (2H, m, 2- and 5-H), 6·67 (2H, m, 1- and 7-*endo*-H), and 7·98 (1H, d, 7-*exo*-H) (Found: C, 63·56; H, 4·2%).

Isomerisation of Compounds (IIa) *and* (IIb).—The 3-isomers from the rearrangement of (IIa) and (IIb) using the procedure described under (a) above were identified from their n.m.r. spectra in a similar way to that for the 3-Ph isomer. 3-Isomer from (IIa) τ (CS_2), 4·19 (1H, d, 4-H), 5·34 (2H, m, 2- and 5-H), 6·50—7·50 (3H, m, 1-, 6-, and 7-*endo*-H), 7·45 (3H, s, Me), 8·20 (1H, m, 7-*exo*-H), and 3-isomer from (IIb) τ (CS_2), 2·78 (4H, ABq, C_6H_4), 3·87 (1H, d, 4-H), 5·05 (1H, d, 2-H), 5·23 (1H, t, 5-H), 6·37—7·30 (3H, m, 1-, 6-, and 7-*endo*-H), 7·63 (3H, s, Me), and 8·10 (1H, m, 7-*exo*-H).

Attempted Isomerisation of Tricarbonyl-(7-endo-*phenylcycloheptatriene*)*chromium*.—A sample of this complex[15] (0·3 g) was heated in refluxing methylcyclohexane (100 ml) for 4 h. Examination by t.l.c. revealed no change and chromatography on a column of alumina gave a single orange band from which the starting material (0·135 g, 45%), m.p. 117—117·5°, was recovered.

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[17] P. L. Pauson and K. H. Todd, *J. Chem. Soc.* (*C*), 1970, 2315.